

ARMY RESEARCH LABORATORY



Tunable Diode Laser Diagnostics for Combustion Species

R. G. Daniel
K. L. McNesby
A. W. Miziolek

ARL-TR-965

February 1996

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION IS UNLIMITED.

19960227 010

DEFENSE QUALITY INSPECTED 1

NOTICES

Destroy this report when it is no longer needed. DO NOT return it to the originator.

Additional copies of this report may be obtained from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161.

The findings of this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.

The use of trade names or manufacturers' names in this report does not constitute indorsement of any commercial product.

| REPORT DOCUMENTATION PAGE | | | Form Approved OMB No. 0704-0188 | |
|--|--|---|---|--|
| Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503. | | | | |
| 1. AGENCY USE ONLY (Leave blank) | | 2. REPORT DATE February 1996 | | 3. REPORT TYPE AND DATES COVERED Final, Sep 93-Sep 95 |
| 4. TITLE AND SUBTITLE Tunable Diode Laser Diagnostics for Combustion Species | | | 5. FUNDING NUMBERS PR: 1L161102AH43 | |
| 6. AUTHOR(S) R. G. Daniel, K. L. McNesby, and A. W. Miziolek | | | | |
| 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army Research Laboratory ATTN: AMSRL-WT-PC Aberdeen Proving Ground, MD 21005-5066 | | | 8. PERFORMING ORGANIZATION REPORT NUMBER ARL-TR-965 | |
| 9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) | | | 10. SPONSORING / MONITORING AGENCY REPORT NUMBER | |
| 11. SUPPLEMENTARY NOTES | | | | |
| 12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution is unlimited. | | | 12b. DISTRIBUTION CODE | |
| 13. ABSTRACT (Maximum 200 words) We report here on work employing tunable diode laser absorption spectroscopy to characterize premixed, low-pressure flames inhibited with halons and halon alternative agents. This characterization is in the form of spatial temperature and species concentration profiles of the flames. We report here the observation of 11 combustion species, including short-lived intermediates CF ₂ O and CF ₃ radical. | | | | |
| 14. SUBJECT TERMS inhibited flames, combustion diagnostics, tunable diode laser | | | 15. NUMBER OF PAGES 28 | |
| | | | 16. PRICE CODE | |
| 17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED | | 18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED | | 19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED |
| | | | | 20. LIMITATION OF ABSTRACT UL |

INTENTIONALLY LEFT BLANK.

ACKNOWLEDGMENTS

The authors would like to acknowledge funding for this project from the Strategic Environmental Research and Development Program.

INTENTIONALLY LEFT BLANK.

TABLE OF CONTENTS

| | <u>Page</u> |
|---------------------------|-------------|
| ACKNOWLEDGMENTS | iii |
| LIST OF FIGURES | vii |
| 1. INTRODUCTION | 1 |
| 2. EXPERIMENTAL | 2 |
| 3. DATA ANALYSIS | 5 |
| 3.1 Carbon Monoxide | 5 |
| 3.2 Other Species | 9 |
| 4. CONCLUSIONS | 14 |
| 5. REFERENCES | 17 |
| DISTRIBUTION LIST | 19 |

INTENTIONALLY LEFT BLANK.

LIST OF FIGURES

| <u>Figure</u> | <u>Page</u> |
|---|-------------|
| 1. Schematic representation of the experimental apparatus | 3 |
| 2. View of the flat flame burner assembly | 4 |
| 3. Sample spectrum of CO in a 20-torr flame | 6 |
| 4. Flame temperature profiles of an uninhibited methane/oxygen flame measured spectroscopically and with fine-wire thermocouples | 8 |
| 5. CO concentration and temperature profiles of 20-torr, stoichiometric, premixed methane/oxygen flames inhibited with 1.0% of the fluoromethanes | 8 |
| 6. Disappearance profiles of methane in a 32-torr inhibited flames relative to an uninhibited flame | 10 |
| 7. Appearance profiles of water in 32-torr inhibited flames relative to an uninhibited flame | 10 |
| 8. Methane disappearance profiles (circles) and water appearance profiles (triangles) for an inhibited flame and a flame inhibited with 1.0% CF_3H | 11 |
| 9. a) Calculated disappearance profiles of the fluoromethanes in a freely propagating, 20-torr methane/oxygen flame. b) Experimental disappearance profiles at the fluoromethanes in burner stabilized, 20-torr methane/oxygen flames | 12 |
| 10. Appearance profiles of CF_2O for 32-torr methane/oxygen/argon flames inhibited with agents at 1.0% total volume | 13 |
| 11. Three-dimensional spectral profile of methane/oxygen/argon flames near 1259.2 cm^{-1} as a function of height above the burner in millimeters | 14 |

INTENTIONALLY LEFT BLANK.

1. INTRODUCTION

The main chemical agents used in fire suppression systems in military vehicles are Halon 1301 and Halon 1211 (CF_2ClBr). In accordance with the Copenhagen amendments to the Montreal Protocol (Fourth Meeting of the Parties to the Montreal Protocol 1992), the production and sale of these compounds, chlorofluorocarbons, and bromochlorofluorocarbons, have been banned because of their role in the catalytic destruction of stratospheric ozone. Furthermore, their usage may be phased out completely before the present stockpile is exhausted. The Army Research Laboratory (ARL) has been involved in a project designed to identify suitable replacement compounds for use in future fire suppression systems, and for inclusion in present fire suppression systems on board Army vehicles.

We have employed tunable diode laser absorption spectroscopy (TDLAS) to characterize low-pressure premixed methane/oxygen/argon flames inhibited with Halon 1301 (CF_3Br) and the Halon alternative compounds FE-13 (CF_3H) and HFC-125 ($\text{C}_2\text{F}_5\text{H}$). This work is part of a larger project designed to help identify replacement fire-suppression compounds for the presently used Halon 1301. The Army's fire suppression need in weapon systems and crew compartments is one of the most stringent. TDLAS has been shown to be a versatile and powerful diagnostic technique to study combustion processes, and is presently being applied to other combustion systems, specifically diffusion flames and nonthermal plasmas.

The aspect of this project reported here is the application of tunable diode lasers as a diagnostic tool to characterize combustion systems. We have studied inhibited low-pressure premixed flames, using the TDLAS technique to measure the flame species' concentration and temperature profiles to characterize the combustion chemistry. The flames are doped with up to 1.0% of a halogenated compound. The results of this study are being used to validate a chemical kinetic mechanism (Westmoreland et al. 1994), which attempts to computationally model the behavior of halogenated flames (Babushok and Tsang 1994).

Tunable diode lasers offer the ability to observe individual ro-vibrational transitions of many flame species in a nonintrusive manner, and thus no perturbation of the combustion system occurs. This ability allows for qualitative and/or quantitative measurement of the production or destruction of a compound as a function of position in the flame. By observing ro-vibrational transitions, a species' temperature and concentration can be extracted from the observed spectra. To date, 11 different flame species (Table 1) have been observed in our laboratory.

Table 1. List of Species Detected using TDLAS

| Species | Frequency (cm^{-1}) | Transition |
|--------------------------------|-----------------------------------|---------------------------|
| CO | 2,020–2,100 | |
| CO ₂ | 2,020–2,100 | ν_3 |
| CH ₄ | 1,240–1,280 | ν_2 and ν_4 dyad |
| H ₂ O | 1,260–1,275 | ν_2 |
| CF ₄ | 1,250–1,280 | ν_3 and $2\nu_4$ |
| CF ₃ H | 1,075–1,100 | ν_2 |
| CF ₂ H ₂ | 1,075–1,120 | ν_3 |
| CF ₃ Br | 1,075–1,120 | ν_1 and $\nu_2+\nu_3$ |
| CF ₃ I | 1,075–1,100 | ν_1 |
| CF ₂ O | 1,250–1,275 | ν_4 |
| | 1,910–1,970 | ν_1 |
| NO | 1,910–1,950 | |

2. EXPERIMENTAL

The details of the experimental apparatus have been previously described in detail (McNesby, Daniel, and Miziolek 1995a) and so will only be briefly discussed here. Figure 1 shows a schematic representation of the three major components of the system: the diode laser as radiation source, the gas handling system, and the data acquisition equipment. Each component will be discussed in the subsequent paragraphs.

The diode laser system (Laser Photonics, Analytics Division, Inc.) consists of a cryogenically cooled laser source, a monochromator, and liquid nitrogen (LN₂) -cooled infrared (IR) detectors. Laser diodes, which are lead salt crystals, produce multimode, monochromatic radiation at cryogenic temperatures (10–100 K) upon application of a small current across the diode. The frequency of the emitted radiation is selected by adjusting the temperature of the applied current to the diode. The linewidth of the radiation is typically 0.0005 cm^{-1} , which allows the detection of individual ro-vibration transitions of the molecules being studied. The emitted radiation passes through the monochromator, selecting the individual mode and thus the frequency of the radiation of interest for the experiment. The IR beam passes through

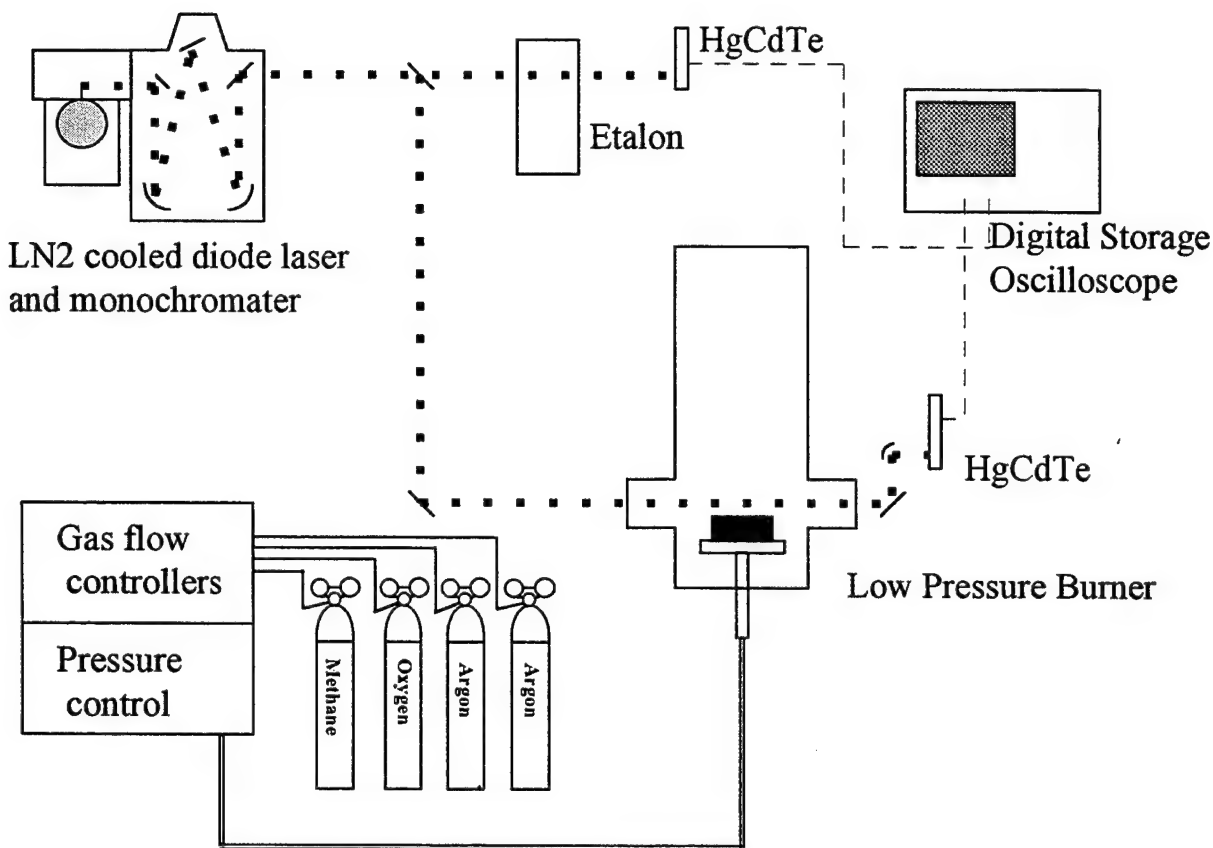


Figure 1. Schematic representation of the experimental apparatus.

a beam splitter, some beam steering and focusing optics, and the burner chamber, and impinges on an LN2-cooled HgCdTe detector. The split portion of the IR radiation passes through a passive confocal etalon that produces fringes as the frequency is scanned. The fringes allow the output of the diode to be monitored for nonlinearities and nonuniformities as the frequency is scanned. Data acquisition electronics receive signals from the IR detector.

The gas handling system consists of flow controllers for each of the gases introduced to the low-pressure burner chamber. A mass flow controller (MKS model 147B) is used to control flow meters (MKS model 2159B) that introduce the fuel (CH_4), oxidizer (O_2 or air), diluent (Ar), shroud gas (Ar), and inhibitor. The stated accuracy is $\pm 1\%$ of the full scale of the flow valve, so the maximum deviation is 0.1 L/min. The reproducibility is quoted as $\pm 0.2\%$ of the reading. We have found the flame characteristics to be very reproducible between experiments with this experimental setup. The inhibitor gas is mixed with the fuel flow at a Swagelok tee. The fuel/inhibitor mix is further mixed with the oxidizer and diluent at a Swagelok cross before entering a final mixing chamber in the burner head.

The low-pressure burner assembly consists of a flat flame burner (McKenna Industries, Inc.) mounted in a cylindrical vacuum chamber (Huntington Vacuum). The flat flame burner (Figure 2) is composed of concentric, sintered stainless steel fits through which the combustion and shroud gases flow. The flame front is supported above the fit. Its height above the fit is determined by the flame velocity, the pressure of the system, and the total flow rate of the gases. The shroud gas flow helps to stabilize the flame and to maintain laminar flow of the premixed gases. A thermocouple cemented to the burner head monitors its temperature. The head is mounted on both horizontal and vertical translation stages that provide for a full range of motion for spatial profiling of flame.

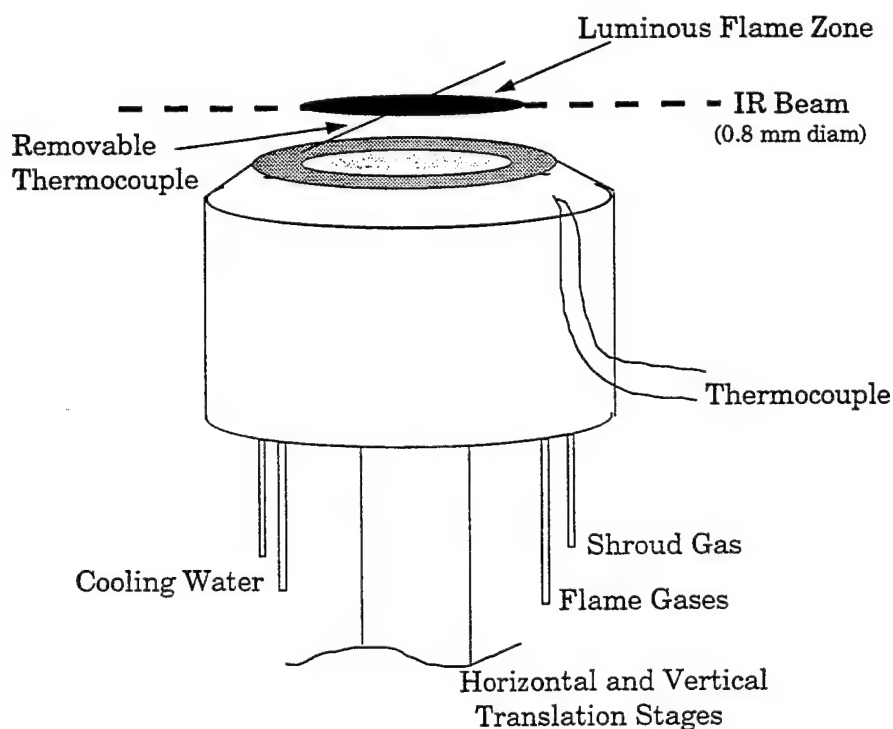


Figure 2. View of the flat flame burner assembly.

The exhaust gases are removed through the top of the low-pressure chamber by a Leybold SV-100 high-volume vacuum pump. They are removed from the top to further assist in maintaining laminar flow of the combustion gases. Coarse control over the chamber pressure is accomplished by a manual butterfly valve. Fine control of the pressure is obtained by a precision needle valve, open to the atmosphere, that is located just upstream to the butterfly valve. This combination of valves allows the pressure to be set and maintained to within several millitorr throughout the course of an experiment. The pressure of the chamber is measured at the base, below the burner head, by a 100-torr range capacitance manometer.

The data acquisition is accomplished using a LeCroy 9360 digital storage oscilloscope. The output of the IR detectors is passed through a preamplifier and then fed into the oscilloscope. The oscilloscope co-adds 500 scans, and then stores the spectrum on a diskette. Since the data are collected as single beam spectra, a background spectrum, consisting of a spectrum with no gases flowing, for each experiment is also collected. The data are transferred to a personal computer, converted to ASCII format, and analyzed to extract the temperature and/or concentration of the species under study.

Flame temperatures are also measured using Pt/10%Pt-Rh fine-wire (5 μm) thermocouples. As the flame temperature exceeds the melting point of platinum, the thermocouples are coated with a refractory mixture of yttrium oxide and beryllium oxide (Kent 1974). The high emissivity of this ceramic sheath reduces the internal temperature of the thermocouple junction. The sheath also minimizes errors caused by platinum-catalyzed reactions at the thermocouple junction.

3. DATA ANALYSIS

The identity of the absorbing species determines the method of analysis of the collected spectra. Carbon monoxide (CO) spectra are analyzed to obtain concentration profiles and to spectroscopically measure the temperature of the flame. The spectra are fit to a mathematical expression of the transmission, and both the concentration and temperature are extracted. The spectra of other flame species are analyzed for concentration information only, relying on the temperature from either the thermocouple or that measured by the CO spectra from that flame. The spectra of each molecule, from the available literature, are used to extract the concentration profiles, either relative concentration between different flames or absolute concentration whenever possible. Both methods are outlined in the subsequent sections.

3.1 Carbon Monoxide. The method known as two-line thermometry (Varghese and Hanson 1980) is used to determine the temperature and CO concentration profile of the flame under study. In this method, the temperature and the concentration of CO are extracted from the observation of two closely lying ro-vibrational transitions of CO originating from excited vibrational states. The flame temperature and CO concentration can be extracted from the ratio of the integrated absorbance of the two transitions.

The experimental transmission spectrum can be mathematically described by the Bouguer-Lambert Law of Absorption (Varghese and Hanson 1980) as:

$$\tau(\nu) = \left(\frac{I}{I_0} \right) = \exp \left(- \left[S_{\nu J}(T) \phi(\nu - \nu_0) L P_x \right] \right) \quad (1)$$

where $S_{\nu J}(T)$ is the line strength of the transition, $\phi(\nu - \nu_0)$ is the line shape function, L is the path length of the absorbing species (nominally set by the dimension of the burner head), and P_x is the partial pressure of absorbing species x . The line strengths ($S_{\nu J}(T)$) of the individual CO ro-vibration transitions have been calculated from a relation referenced to the literature value of the fundamental band strength of the transition (Varghese and Hanson 1980). The normalized single beam spectrum is fit to the following:

$$\tau(\nu) = \sum_i \exp \left(- \left[\alpha_i(T) V_i(a, \chi) \right] \right) + \Delta \quad (2)$$

where $\alpha_i(T)$ is the product of the line strength of the i^{th} transition with the pressure of the absorbing species, $V_i(a, \chi)$ is the Voigt function with the Voigt parameter and $\chi = (\nu - \nu_0)/\nu_D$, and Δ is a cubic baseline correction to account for the nonlinear output of the diode laser. The summation refers to the individual transitions present in the frequency range of the spectrum. A sample spectrum of CO is shown in Figure 3. The summation in equation 2 for this spectrum would thus include the CO P18(2,1) and the CO P12(3,2) transitions.

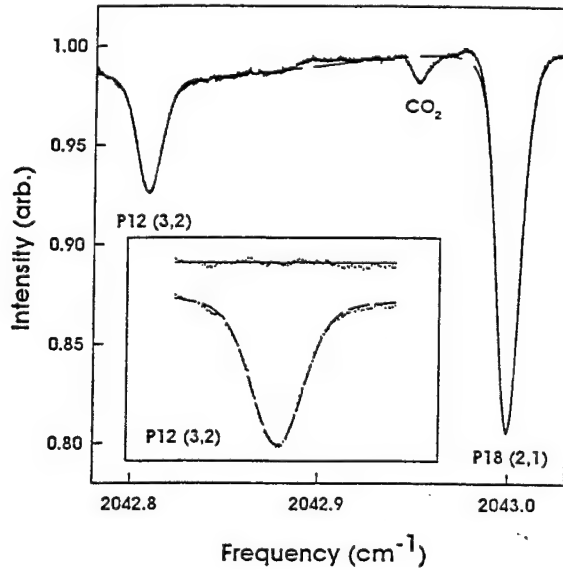


Figure 3. Sample spectrum of CO in a 20-torr flame. The inset shows a blowup view of the data plus fit, and the residual of the fit, of the P12 (3, 2) transition.

The observed CO spectrum is fit to the above equations using a nonlinear least-squares fitting routine (Bevington 1969). The Voigt profile is calculated using a summation approximation to the complex error probability function (Humlíček 1979). T , α_i , a broadening parameter, a frequency shift for each transition, and the baseline parameters are the variables in this program. The temperature of the species being measured is determined from the ratio of the observed α_i by comparing this to values of the ratio of the calculated line strengths:

$$F(T) = \frac{S_{vJ}^{\text{II}}(T)}{S_{vJ}^{\text{I}}(T)} = \frac{\alpha^{\text{II}}(T)}{\alpha^{\text{I}}(T)}. \quad (3)$$

The pressure of the absorbing species is obtained from the definition of the α_i once the temperature has been calculated:

$$P_x = \frac{\alpha^{\text{I}}(T)}{S_{vJ}^{\text{I}}(T)}. \quad (4)$$

The calculated line strength values are used to construct the $F(T)$ found in equation 3. The goodness of the fit is measured by the chi squared test. Data sets for each flame and position within the flame are collected four times, and the results of the four sets are examined statistically for inconsistencies before being averaged to produce the final average value of temperature and concentration used as characteristic of the flame.

In a previous study, the final values of spectroscopically measured flame temperatures were consistently lower than the values measured by fine-wire thermocouples. In this study, the distribution of CO across the burner head was measured using tomographic analysis (McNesby, Daniel, and Miziolek 1995a). The flame temperatures obtained from the spectroscopic measurements are corrected to account for absorption by CO lying outside the burner region. The reduced absorbance of the individual transitions translates to a higher temperature than originally calculated. This is illustrated in Figure 4, in which thermocouple and spectroscopic temperatures (both corrected and uncorrected) are included. Figure 5 presents the CO concentration and temperature profiles of methane/oxygen flames inhibited with 1.0% of the fluoromethanes analyzed using two-line thermometry. It is readily seen from the figure that each agent produces unique behavior in the flame.

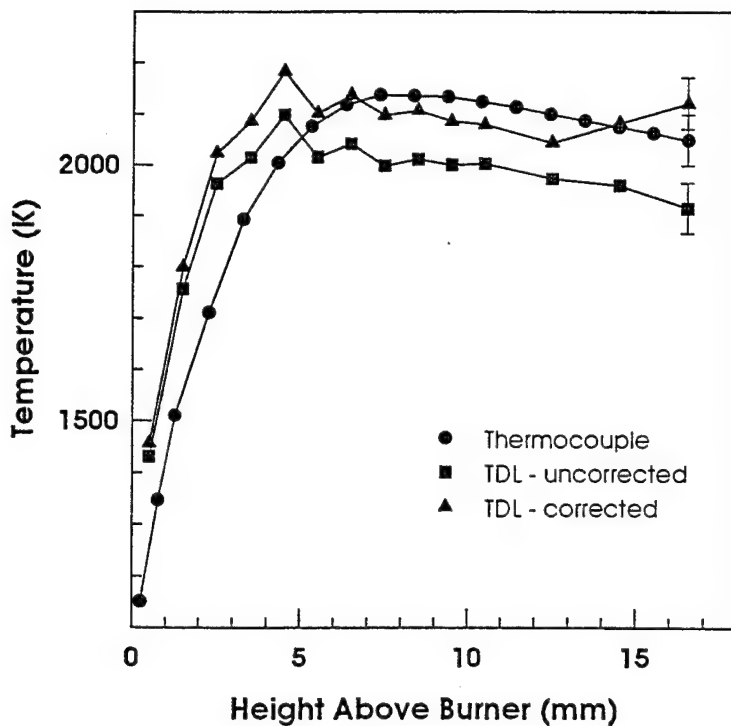


Figure 4. Flame temperature profiles of an inhibited methane/oxygen flame measure spectroscopically and with fine wire thermocouples.

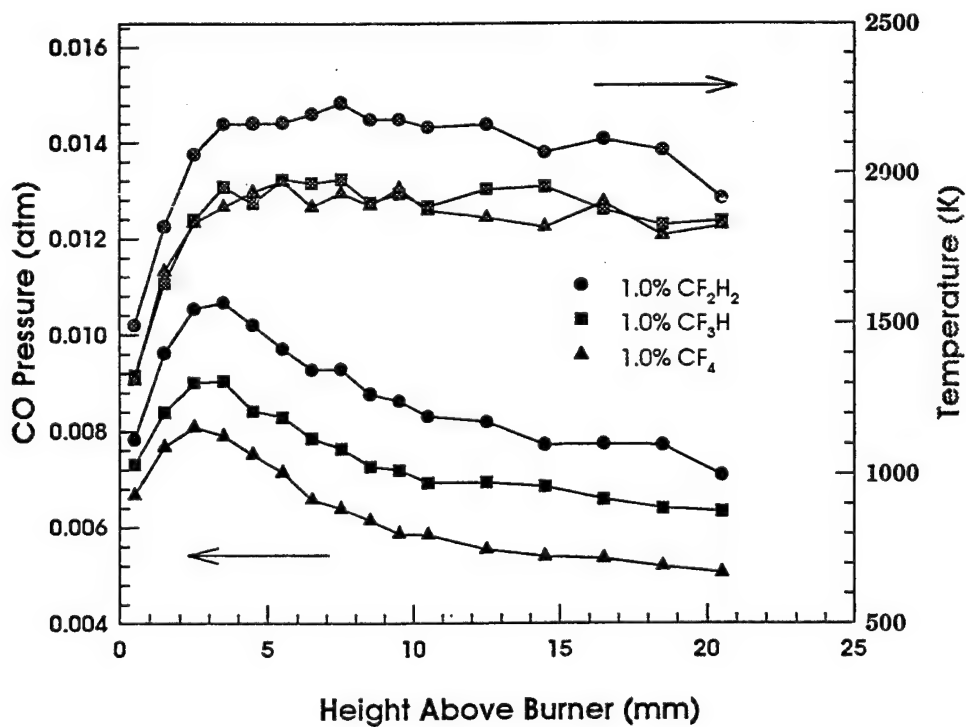


Figure 5. CO concentration and temperature profiles of 20-torr, stoichiometric, premixed methane/oxygen flames inhibited with 1.0% of the fluoromethanes.

3.2 Other Species. The concentration profiles of the other species, observed using IR absorption spectroscopy and employing the LeCroy 9360 digital oscilloscope, are analyzed by either of two methods. The first method obtains relative concentrations of the species by integrating the normalized absorbance of a specific transition of the molecule being studied. The spectrum of one or more individual ro-vibration transitions is collected for flames doped with each of the inhibiting compounds being studied. The spectrum is then normalized by taking a ratio with respect to a background spectrum collected with no gas flow. This normalization procedure accounts for differences in the diode laser output power, which varies day to day. The area of the normalized spectrum is then determined by numerical integration before being compared with the values from the other flames.

These relative intensities can be compared for flames containing different inhibitor and different inhibitor amounts. Figures 6 and 7 show the relative disappearance profiles of CH_4 and appearance profiles of H_2O for both an uninhibited flame and flames doped with 1% of the inhibitors Halon 1301 (CF_3Br), HFC-125 ($\text{C}_2\text{F}_5\text{H}$), and FE-13 (CF_3H). The pressure of these flames was 32 torr. As seen in Figures 6 and 7, the effects of the inhibiting agent on the relative population of the observed species are unique to each agent. For example, in Figure 6, the lowest trace is the disappearance profile of CH_4 in an uninhibited flame. In the other three flames, the amount of methane is higher at each position above the burner, indicating that the methane is reacting at a slower rate than in the uninhibited flame. Thus, the rate of disappearance of CH_4 is slower in each of the doped flames, as evidenced by the higher relative population of CH_4 in the inhibited flames. However, the rate of appearance of H_2O does not decrease for all the agents. Halon 1301 actually increases the rate of appearance. It is this type of information, the differences in the chemistry of the flame, which is used in making qualitative comparisons with the modeling results. Figure 8 is another illustration of the changes in the characteristics of the flames. In a 20-torr flame, the flame front's position, stabilized above the burner as a function of the flame speed, visibly shifts, indicating a reduction of the flame speed. The change in the flame front position is another example of a qualitative effect that can be compared to modeling results.

The second method, presently under development, determines the absolute concentration of the species of interest by using the line strength of the transition examined. This approach requires both the identification of the transition and the species temperature. The transition is identified by comparison with exact line positions from the literature, and the temperature of the species is determined either from the fine-wire thermocouples or spectroscopically, where the flame temperature is assumed to equal the species temperature. By fitting a mathematical model of the lineshape of the transition, an absolute concentration

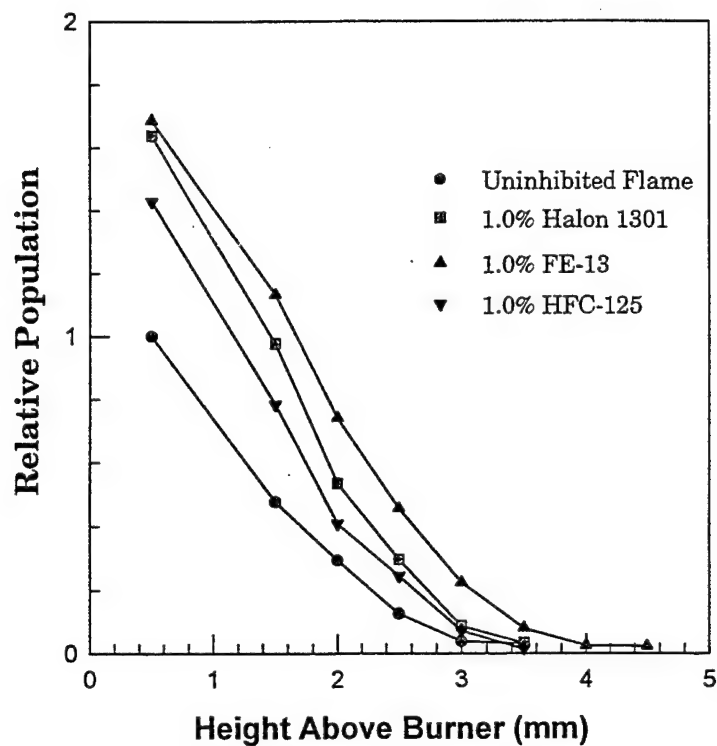


Figure 6. Disappearance profiles of methane in a 32-torr inhibited flames relative to an inhibited flame.

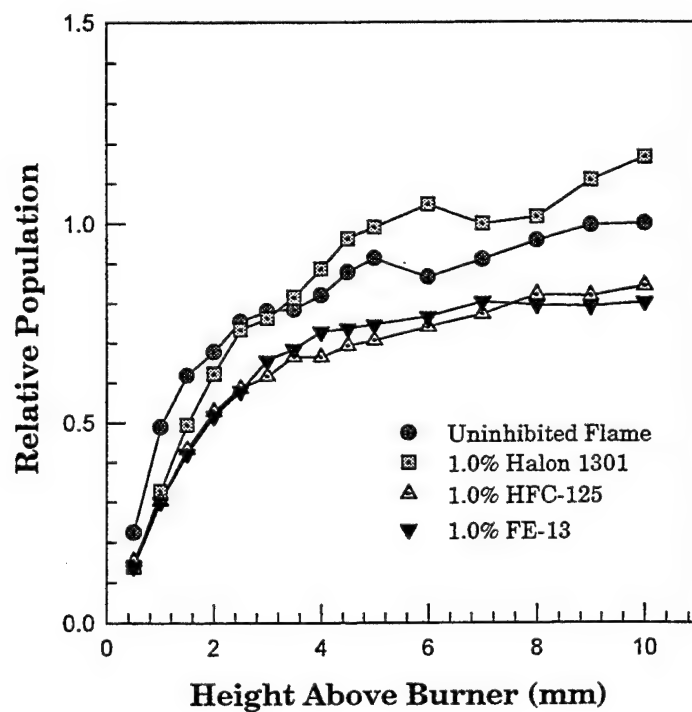


Figure 7. Appearance profiles of water in 32-torr inhibited flames relative to an inhibited flame.

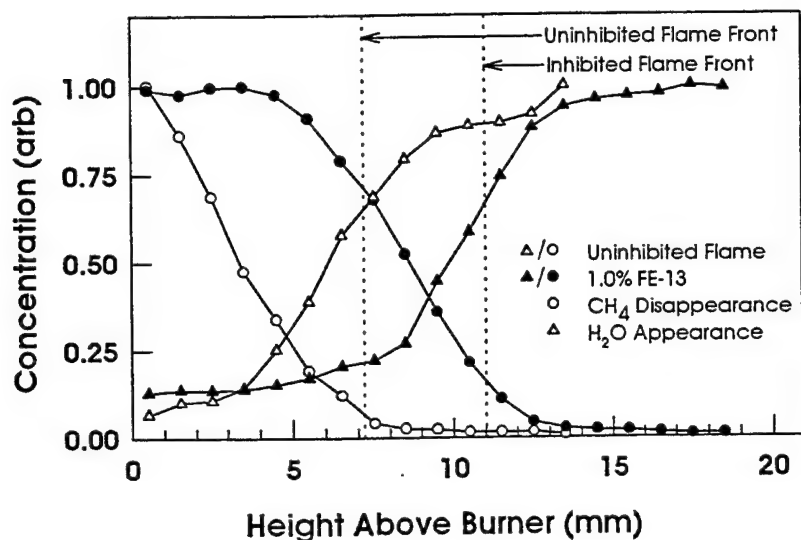


Figure 8. Methane disappearance profiles (circles) and water appearance profiles (triangles) for an inhibited flame and a flame inhibited with 1.0% CF_3H . The shift in the flame front away from the burner is attributed to a decrease in the flame speed.

of the species can then be extracted. The molecules presently being studied for absolute concentration using this method are CH_4 , H_2O , and CF_2O .

Even without absolute concentrations for all species observed, the information obtained has proven useful for the validation of the chemical kinetic mechanism describing fluorine chemistry in flames (Linteris and Gmurczyk 1995; Babushok et al. 1995). Figure 9a shows the calculated disappearance profiles of three fluoromethane agents in a 20-torr, freely propagating methane/air flame. Figure 9b shows the observed relative disappearance profiles of the same agents in a 20-torr burner stabilized methane/oxygen flame. Qualitative agreement is easily seen, though the calculations are not yet directly comparable. Work continues on the modeling to incorporate the experimental conditions to allow for direct comparison with the experimental results.

Figure 10 presents the appearance profiles of CF_2O in flames inhibited with two candidate halon replacement compounds, FE-13 (CF_3H) and HFC-125 ($\text{C}_2\text{F}_5\text{H}$), and with Halon 1301 (CF_3Br) for comparison. The profiles show that more CF_2O , a toxic byproduct of the combustion process of fluorine-containing flames, is produced by both alternate agents than by Halon 1301. Other qualitative differences in the activity of these agents are illustrated in Figures 11a-d, which show an uninhibited flame and flames inhibited with 1.0% of the three agents near $1,259.2\text{ cm}^{-1}$. The most obvious change is the

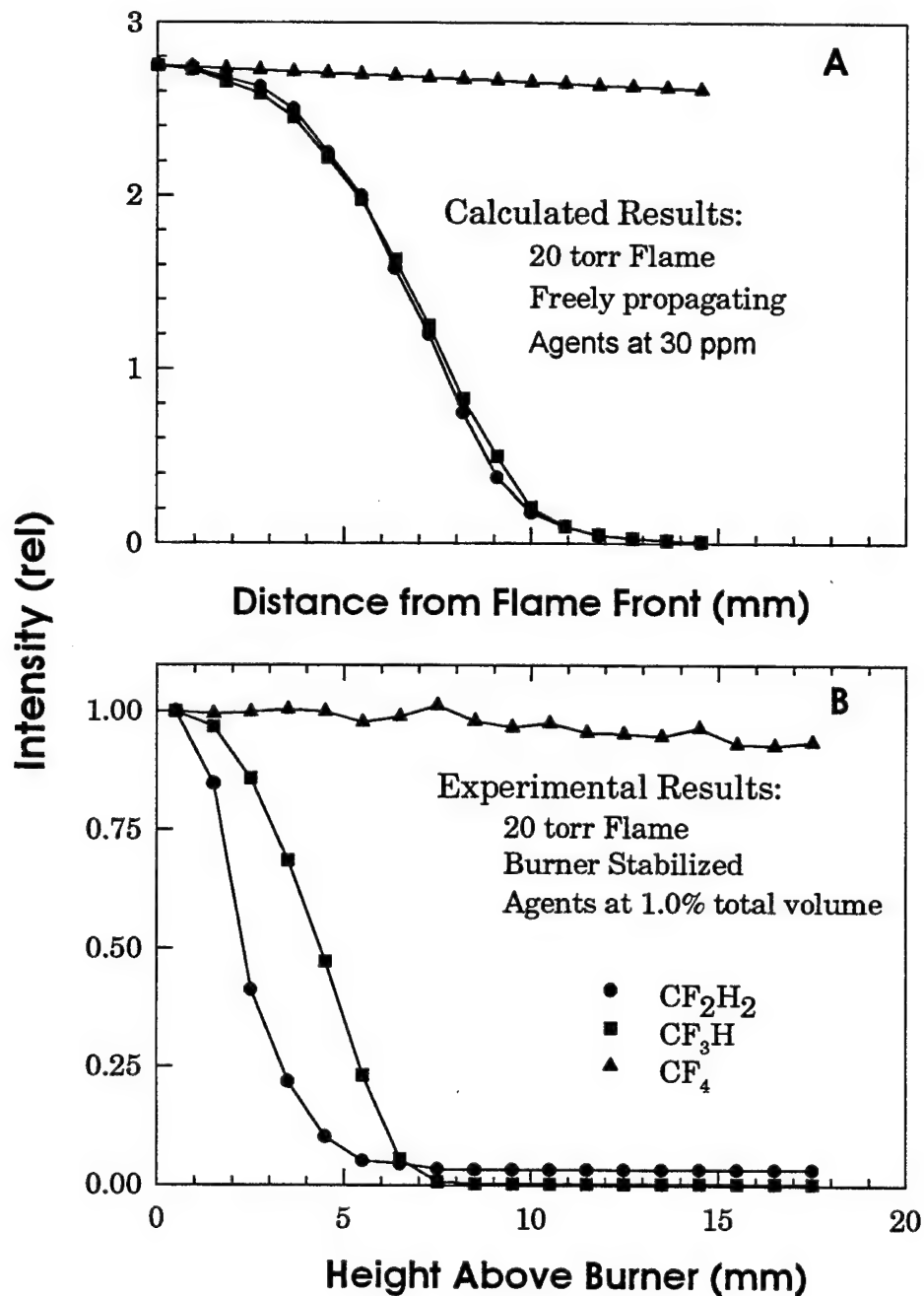


Figure 9. A) Calculated disappearance profiles of the fluoromethanes in a freely propagating, 20-torr methane/oxygen flame. The flame front is at 0 mm. B) Experimental disappearance profiles at the fluoromethanes in burner stabilized, 20-torr methane/ oxygen flames. The flame front is at 4 mm for all three flames.

intensity of the two water transitions. (Each of the spectra in Figure 11 is a scan of 0.25 cm^{-1} ; yet, in the narrow region, transitions of three different molecules are readily observed and easily separated.) The intensity of the methane transition also increases upon the addition of all three agents. This change occurs because the agents cause a change in the species temperature within the flame, thus changing the population distribution among the molecular energy levels. Also shown are the differing amounts of CF_2O produced. Figure 11 also clearly illustrates the strength of the TDLAS technique in observing individual molecules in spectrally congested regions.

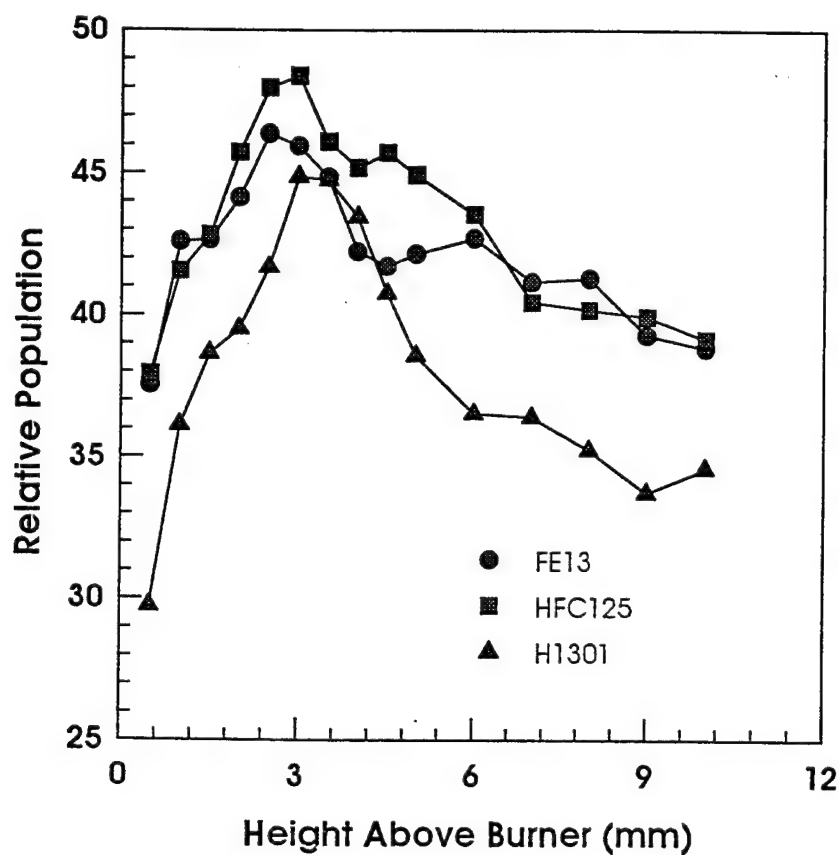


Figure 10. Appearance profiles of CF_2O for 32-torr methane/oxygen/argon flames inhibited with agents at 1.0% total volume.

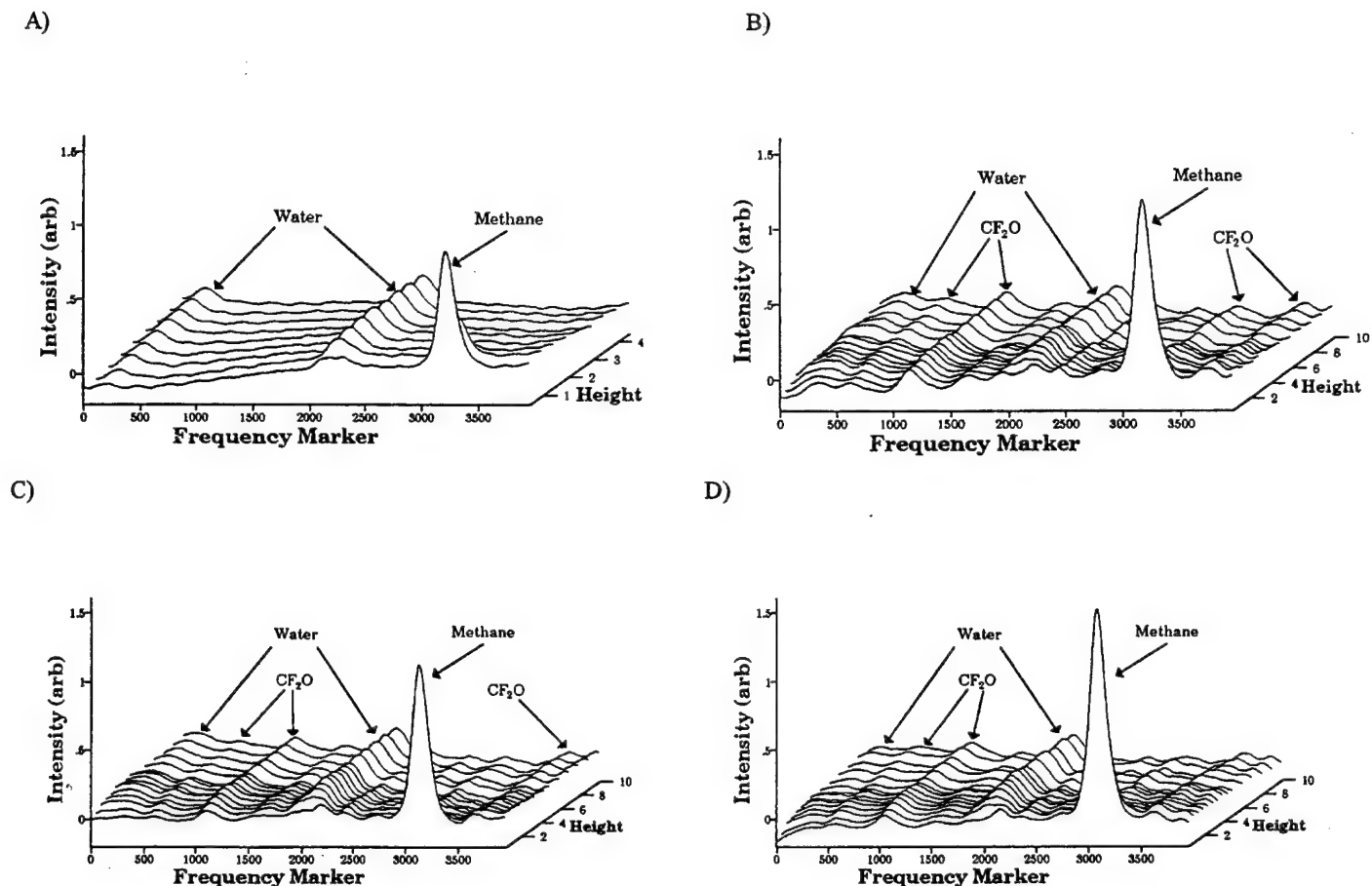


Figure 11. Three-dimensional spectral profile of methane/oxygen/argon flames at $1,259.2\text{ cm}^{-1}$ as a function of height above the burner in millimeters. A) Inhibited flame. B) Flame inhibited with 1.0% HFC-125. C) Flame inhibited with 1.0% FE-13. D) Flame inhibited with 1.0% Halon 1301.

4. CONCLUSIONS

We have obtained both qualitative and quantitative concentration profiles of combustion species in low-pressure, premixed flames inhibited with halon-alternate compounds and with Halon 1301. Flame temperature profiles have also been measured both with fine-wire thermocouples and spectroscopically using the method of two-line thermometry. The data are presently being used in the validation of a

chemical kinetic mechanism that describes halogenated flames. This study has also shown the versatility of TDLAS in the characterization of combustion systems where a line-of-sight technique can be applied, and with the availability of IR transmitting fibers, virtually any combustion system can be analyzed using tunable diode lasers. We have observed 11 flame species present in the combustion system, and are continuing to expand this number.

Through this project, we are expanding the understanding of the fundamental processes that govern flame inhibition. This work continues along the following paths: the inclusion of other combustion species, including important radical species ($\text{CF}_2\cdot$ and $\text{CF}_3\cdot$) (McNesby, Daniel, and Miziolek 1995b) the application of TDLAS to diffusion flames (McNesby et al. 1996) coupling with modeling (Smooke 1994, 1995) of these flames, and the inclusion of a room temperature near-IR laser system for the detection of the acid gas HF in combustion systems. The use of near-IR lasers for acid gas detection has shown promise as another technique for monitoring combustion processes and the byproducts of halogenated flames (Bomse et al. 1992).

INTENTIONALLY LEFT BLANK.

6. REFERENCES

- Babushok, V., and W. Tsang. Private communication. National Institute of Science and Technology, Gaithersburg, MD, 1994.
- Babushok, V., D. R. F. Burgess, Jr., G. Linteris, W. Tsang, and A. W. Miziolek. "Modeling of Hydrogen Fluoride Formation from Flame Suppressants During Combustion." Proceedings, Halon Options Technical Working Conference, Albuquerque, NM, May 1995.
- Bevington, P. R. Data Reduction and Error Analysis for the Physical Sciences. New York: McGraw-Hill, 1969.
- Bomse, D. S., D. C. Houde, D. B. Oh, J. A. Silver, and A. C. Stanton. "Diode Laser Spectroscopy for On-Line Chemical Analysis." SPIE, vol. 1681, Optically Based Methods for Process Analysis, p. 138, 1992.
- Fourth Meeting of the Parties to the Montreal Protocol. "Substances that Deplete the Ozone Layer." 23-25 November 1992. Copenhagen. Doc. no. UNEP/OzL.Pro.4/15 (Nairobi:UNEP,1992),32. The full text of the London and Copenhagen amendments to the Montreal Protocol on Substances that Deplete the Ozone Layer, with the Montreal Protocol attached as an appendix can be found at gopher://gopher.law.cornell.edu/00/foreign/fletcher/MONTREAL-1992.txt.
- Humlíček, J. "An Efficient Method for Evaluation of the Complex Probability Function: The Voigt Function and Its Derivatives." Journal of Quantitative Spectroscopy and Radiative Transfer, vol. 21, p. 309, 1979.
- Kent, J. H. "A Noncatalytic Coating for Platinum-Rhodium Thermocouples." Combustion and Flame, vol. 14, p. 270, 1974.
- Linteris, G., and G. Gmurczyk. "Parametric Studies of Hydrogen Fluoride Formation in Suppressed Flames." Proceedings, Halon Options Technical Working Conference, Albuquerque, NM, May 1995.
- McNesby, K. L., R. G. Daniel, and A. W. Miziolek. "Tomographic Analysis of CO Absorption in a Low-Pressure Flame." Applied Optics, vol. 34, p. 3318, 1995a.
- McNesby, K. L., R. G. Daniel, and A. W. Miziolek. "Frequency Modulated Diode Laser Spectroscopy for Detection of Combustion Intermediates." Proceedings of the JANNAF 32nd Combustion Subcommittee Meeting, 23-27 October 1995b.
- McNesby, K. L., R. G. Daniel, J. M. Widder, and A. W. Miziolek. "Spectroscopic Investigation of Atmospheric Diffusion Flames Inhibited by Halons and Their Alternatives." Applied Spectroscopy, (in press) to be published January 1996.
- Smooke, M. Private communication. Yale University, New Haven, CT, 1994, 1995.
- Varghese, P. L., and R. K. Hanson. "Tunable Infrared Diode Laser Measurements of Line Strengths and Collision Widths of $^{12}\text{C}^{16}\text{O}$ at Room Temperature." Journal of Quantitative Spectroscopy & Radiative Transfer, vol. 24, p. 279, 1980.

Westmoreland, P. R., D. R. F. Burgess, Jr., W. Tsang, and M. R. Zachariah. "Fluoromethane Chemistry and Its Role in Flames Suppression." Proceedings of the 25th Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA, 1994.

**NO. OF
COPIES**

ORGANIZATION

2 DEFENSE TECHNICAL INFO CTR
ATTN DTIC DDA
8725 JOHN J KINGMAN RD
STE 0944
FT BELVOIR VA 22060-6218

1 DIRECTOR
US ARMY RESEARCH LAB
ATTN AMSRL OP SD TA
2800 POWDER MILL RD
ADELPHI MD 20783-1145

3 DIRECTOR
US ARMY RESEARCH LAB
ATTN AMSRL OP SD TL
2800 POWDER MILL RD
ADELPHI MD 20783-1145

1 DIRECTOR
US ARMY RESEARCH LAB
ATTN AMSRL OP SD TP
2800 POWDER MILL RD
ADELPHI MD 20783-1145

ABERDEEN PROVING GROUND

5 DIR USARL
ATTN AMSRL OP AP L (305)

| <u>NO. OF COPIES</u> | <u>ORGANIZATION</u> |
|--------------------------|--|
| 1 | HQDA ATTN SARD TT DR F MILTON PENTAGON WASHINGTON DC 20310-0103 |
| 1 | HQDA ATTN SARD TT MR J APPEL PENTAGON WASHINGTON DC 20310-0103 |
| 1 | HQDA OASA RDA ATTN DR C H CHURCH PENTAGON ROOM 3E486 WASHINGTON DC 20310-0103 |
| 4 | COMMANDER US ARMY RESEARCH OFFICE ATTN R GHIRARDELLI D MANN R SINGLETON R SHAW P O BOX 12211 RSCH TRNGLE PK NC 27709-2211 |
| 1 | DIRECTOR ARMY RESEARCH OFFICE ATTN AMXRO RT IP LIB SERVICES P O BOX 12211 RSCH TRNGLE PK NC 27709-2211 |
| 2 | COMMANDER US ARMY ARDEC ATTN SMCAR AEE B D S DOWNS PCTNY ARSNL NJ 07806-5000 |
| 2 | COMMANDER US ARMY ARDEC ATTN SMCAR AEE J A LANNON PCTNY ARSNL NJ 07806-5000 |
| 1 | COMMANDER US ARMY ARDEC ATTN SMCAR AEE BR L HARRIS PCTNY ARSNL NJ 07806-5000 |
| 2 | COMMANDER US ARMY MISSILE COMMAND ATTN AMSMI RD PR E A R MAYKUT AMSMI RD PR P R BETTS REDSTONE ARSENAL AL |

| <u>NO. OF COPIES</u> | <u>ORGANIZATION</u> |
|--------------------------|---|
| 1 | OFFICE OF NAVAL RESEARCH DEPARTMENT OF THE NAVY ATTN R S MILLER CODE 432 800 N QUINCY STREET ARLINGTON VA 22217 |
| 1 | COMMANDER NAVAL AIR SYSTEMS COMMAND ATTN J RAMNARACE AIR 54111C WASHINGTON DC 20360 |
| 2 | COMMANDER NAVAL SURFACE WARFARE CENTER ATTN R BERNECKER R 13 G B WILMOT R 16 SILVER SPRING MD 20903-5000 |
| 5 | COMMANDER NAVAL RESEARCH LABORATORY ATTN M C LIN J MCDONALD E ORAN J SHNUR R J DOYLE CODE 6110 WASHINGTON DC 20375 |
| 2 | COMMANDER NAVAL WEAPONS CENTER ATTN T BOGGS CODE 388 T PARR CODE 3895 CHINA LAKE CA 93555-6001 |
| 1 | SUPERINTENDENT NAVAL POSTGRADUATE SCHOOL DEPT OF AERONAUTICS ATTN D W NETZER MONTEREY CA 93940 |
| 3 | AL LSCF ATTN R CORLEY R GEISLER J LEVINE EDWARDS AFB CA 93523-5000 |
| 1 | AFOSR ATTN J M TISHKOFF BOLLING AIR FORCE BASE WASHINGTON DC 20332 |

NO. OF
COPIES ORGANIZATION

1 OSD SDIO IST
ATTN L CAVENY
PENTAGON
WASHINGTON DC 20301-7100

1 COMMANDANT
USAFAS
ATTN ATSF TSM CN
FORT SILL OK 73503-5600

1 UNIV OF DAYTON RSCH INSTITUTE
ATTN D CAMPBELL
AL PAP
EDWARDS AFB CA 93523

1 NASA
LANGLEY RESEARCH CENTER
ATTN G B NORTHAM MS 168
LANGLEY STATION
HAMPTON VA 23365

4 NATIONAL BUREAU OF STANDARDS
US DEPARTMENT OF COMMERCE
ATTN J HASTIE
M JACOX
T KASHIWAGI
H SEMERJIAN
WASHINGTON DC 20234

2 DIRECTOR
LAWRENCE LIVERMORE NATIONAL LAB
ATTN C WESTBROOK
W TAO MS L 282
P O BOX 808
LIVERMORE CA 94550

1 DIRECTOR
LOS ALAMOS NATIONAL LAB
ATTN B NICHOLS T7 MS B284
P O BOX 1663
LOS ALAMOS NM 87545

2 PRINCETON COMBUSTION
RESEARCH LABORATORIES INC
ATTN N A MESSINA
M SUMMERFIELD
PRINCETON CORPORATE PLAZA
BLDG IV SUITE 119
11 DEERPARK DRIVE
MONMOUTH JUNCTION NJ 08852

NO. OF
COPIES ORGANIZATION

3 DIRECTOR
SANDIA NATIONAL LABORATORIES
DIVISION 8354
ATTN S JOHNSTON
P MATTERN
D STEPHENSON
LIVERMORE CA 94550

1 BRIGHAM YOUNG UNIVERSITY
DEPT OF CHEMICAL ENGINEERING
ATTN M W BECKSTEAD
PROVO UT 84058

1 CALIFORNIA INSTITUTE OF TECH
JET PROPULSION LABORATORY
ATTN L STRAND MS 125 224
4800 OAK GROVE DRIVE
PASADENA CA 91109

1 CALIFORNIA INSTITUTE OF TECHNOLOGY
ATTN F E C CULICK MC 301 46
204 KARMAN LAB
PASADENA CA 91125

1 UNIVERSITY OF CALIFORNIA
LOS ALAMOS SCIENTIFIC LAB
P O BOX 1663 MAIL STOP B216
LOS ALAMOS NM 87545

1 UNIVERSITY OF CALIFORNIA BERKELEY
CHEMISTRY DEPARMENT
ATTN C BRADLEY MOORE
211 LEWIS HALL
BERKELEY CA 94720

1 UNIVERSITY OF CALIFORNIA SAN DIEGO
ATTN F A WILLIAMS
AMES B010
LA JOLLA CA 92093

2 UNIV OF CALIFORNIA SANTA BARBARA
QUANTUM INSTITUTE
ATTN K SCHOFIELD
M STEINBERG
SANTA BARBARA CA 93106

1 UNIV OF COLORADO AT BOULDER
ENGINEERING CENTER
ATTN J DAILY
CAMPUS BOX 427
BOULDER CO 80309-0427

| <u>NO. OF COPIES</u> | <u>ORGANIZATION</u> |
|--------------------------|---|
| 3 | UNIV OF SOUTHERN CALIFORNIA DEPT OF CHEMISTRY ATTN R BEAUDET S BENSON C WITTIG LOS ANGELES CA 90007 |
| 1 | CORNELL UNIVERSITY DEPARTMENT OF CHEMISTRY ATTN T A COOL BAKER LABORATORY ITHACA NY 14853 |
| 1 | UNIVERSITY OF DELAWARE CHEMISTRY DEPARTMENT ATTN T BRILL NEWARK DE 19711 |
| 1 | UNIVERSITY OF FLORIDA DEPT OF CHEMISTRY ATTN J WINEFORDNER GAINESVILLE FL 32611 |
| 3 | GEORGIA INSTITUTE OF TECHNOLOGY SCHOOL OF AEROSPACE ENGINEERING ATTN E PRICE W C STRAHLE B T ZINN ATLANTA GA 30332 |
| 1 | UNIVERSITY OF ILLINOIS DEPT OF MECH ENG ATTN H KRIER 144MEB 1206 W GREEN ST URBANA IL 61801 |
| 1 | THE JOHNS HOPKINS UNIV CPIA ATTN T W CHRISTIAN 10630 LITTLE PATUXENT PKWY SUITE 202 COLUMBIA MD 21044-3200 |
| 1 | UNIVERSITY OF MICHIGAN GAS DYNAMICS LAB ATTN G M FAETH AEROSPACE ENGINEERING BLDG ANN ARBOR MI 48109-2140 |
| 1 | UNIVERSITY OF MINNESOTA DEPT OF MECHANICAL ENGINEERING ATTN E FLETCHER MINNEAPOLIS MN 55455 |

| <u>NO. OF COPIES</u> | <u>ORGANIZATION</u> |
|--------------------------|---|
| 4 | PENNSYLVANIA STATE UNIVERSITY DEPT OF MECHANICAL ENGINEERING ATTN K KUO M MICCI S THYNELL V YANG UNIVERSITY PARK PA 16802 |
| 2 | PRINCETON UNIVERSITY FORRESTAL CAMPUS LIBRARY ATTN K BREZINSKY I GLASSMAN P O BOX 710 PRINCETON NJ 08540 |
| 1 | PURDUE UNIVERSITY SCHL OF AERONAUTICS & ASTRONAUTICS ATTN J R OSBORN GRISSOM HALL WEST LAFAYETTE IN 47906 |
| 1 | PURDUE UNIVERSITY DEPARTMENT OF CHEMISTRY ATTN E GRANT WEST LAFAYETTE IN 47906 |
| 2 | PURDUE UNIVERSITY SCHL OF MECHANICAL ENGNRNG ATTN N M LAURENDEAU S N B MURTHY TSPC CHAFFEE HALL WEST LAFAYETTE IN 47906 |
| 1 | RENSSELAER POLYTECHNIC INST DEPT OF CHEMICAL ENGINEERING ATTN A FONTUN TROY NY 12181 |
| 1 | STANFORD UNIVERSITY DEPT OF MECHANICAL ENGINEERING ATTN R HANSON STANFORD CA 94305 |
| 1 | UNIVERSITY OF TEXAS DEPT OF CHEMISTRY ATTN W GARDINER AUSTIN TX 78712 |
| 1 | VA POLYTECH INST AND STATE UNIV ATTN J A SCHETZ BLACKSBURG VA 24061 |

| <u>NO. OF COPIES</u> | <u>ORGANIZATION</u> |
|--------------------------|--|
| 1 | APPLIED COMBUSTION TECHNOLOGY INC ATTN A M VARNEY P O BOX 607885 ORLANDO FL 32860 |
| 2 | APPLIED MECHANICS REVIEWS ASME ATTN R E WHITE & A B WENZEL 345 E 47TH STREET NEW YORK NY 10017 |
| 1 | TEXTRON DEFENSE SYSTEMS ATTN A PATRICK 2385 REVERE BEACH PARKWAY EVERETT MA 02149-5900 |
| 1 | BATTELLE TWSTIAC 505 KING AVENUE COLUMBUS OH 43201-2693 |
| 1 | COHEN PROFESSIONAL SERVICES ATTN N S COHEN 141 CHANNING STREET REDLANDS CA 92373 |
| 1 | EXXON RESEARCH & ENG CO ATTN A DEAN ROUTE 22E ANNANDALE NJ 08801 |
| 1 | GENERAL APPLIED SCIENCE LABS INC 77 RAYNOR AVENUE RONKONKAMA NY 11779-6649 |
| 1 | GENERAL ELECTRIC ORDNANCE SYSTEMS ATTN J MANDZY 100 PLASTICS AVENUE PITTSFIELD MA 01203 |
| 1 | GENERAL MOTORS RSCH LABS PHYSICAL CHEMISTRY DEPARTMENT ATTN T SLOANE WARREN MI 48090-9055 |
| 2 | HERCULES INC ATTN W B WALKUP E A YOUNT P O BOX 210 ROCKET CENTER WV 26726 |

| <u>NO. OF COPIES</u> | <u>ORGANIZATION</u> |
|--------------------------|--|
| 1 | HERCULES INC ATTN R V CARTWRIGHT 100 HOWARD BLVD KENVIL NJ 07847 |
| 1 | ALLIANT TECHSYSTEMS INC MARINE SYSTEMS GROUP ATTN D E BRODEN MS MN50 2000 600 2ND STREET NE HOPKINS MN 55343 |
| 1 | ALLIANT TECHSYSTEMS INC ATTN R E TOMPKINS MN 11 2720 600 SECOND ST NORTH HOPKINS MN 55343 |
| 1 | IBM CORPORATION RESEARCH DIVISION ATTN A C TAM 5600 COTTLE ROAD SAN JOSE CA 95193 |
| 1 | IIT RESEARCH INSTITUTE ATTN R F REMALY 10 WEST 35TH STREET CHICAGO IL 60616 |
| 1 | LOCKHEED MISSILES & SPACE CO ATTN GEORGE LO 3251 HANOVER STREET DEPT 52 35 B204 2 PALO ALTO CA 94304 |
| 1 | OLIN ORDNANCE ATTN V MCDONALD LIBRARY P O BOX 222 ST MARKS FL 32355-0222 |
| 1 | PAUL GOUGH ASSOCIATES INC ATTN P S GOUGH 1048 SOUTH STREET PORTSMOUTH NH 03801-5423 |
| 1 | HUGHES AIRCRAFT COMPANY ATTN T E WARD PO BOX 11337 TUCSON AZ 85734-1337 |

| <u>NO. OF COPIES</u> | <u>ORGANIZATION</u> |
|--------------------------|---|
| 1 | SCIENCE APPLICATIONS INC ATTN R B EDELMAN 23146 CUMORAH CREST WOODLAND HILLS CA 91364 |
| 3 | SRI INTERNATIONAL ATTN G SMITH D CROSLEY D GOLDEN 333 RAVENSWOOD AVENUE MENLO PARK CA 94025 |
| 1 | STEVENS INSTITUTE OF TECH DAVIDSON LABORATORY ATTN R MCALEVY III HOBOKEN NJ 07030 |
| 1 | SVERDRUP TECHNOLOGY INC LERC GROUP ATTN R J LOCKE MS SVR 2 2001 AEROSPACE PARKWAY BROOK PARK OH 44142 |
| 1 | SVERDRUP TECHNOLOGY INC ATTN J DEUR 2001 AEROSPACE PARKWAY BROOK PARK OH 44142 |
| 3 | THIOKOL CORPORATION ELKTON DIVISION ATTN R BIDDLE R WILLER TECH LIB P O BOX 241 ELKTON MD 21921 |
| 3 | THIOKOL CORPORATION WASATCH DIVISION ATTN S J BENNETT P O BOX 524 BRIGHAM CITY UT 84302 |
| 1 | UNITED TECHNOLOGIES RSCH CENTER ATTN A C ECKBRETH EAST HARTFORD CT 06108 |
| 1 | UNITED TECHNOLOGIES CORP CHEMICAL SYSTEMS DIVISION ATTN R R MILLER P O BOX 49028 SAN JOSE CA 95161-9028 |

| <u>NO. OF COPIES</u> | <u>ORGANIZATION</u> |
|--------------------------|---|
| 1 | UNIVERSAL PROPULSION COMPANY ATTN H J MCSPADDEN 25401 NORTH CENTRAL AVENUE PHOENIX AZ 85027-7837 |
| 1 | VERITAY TECHNOLOGY INC ATTN E B FISHER 4845 MILLERSPORT HIGHWAY EAST AMHERST NY 14051-0305 |
| 1 | FREEDMAN ASSOCIATES ATTN E FREEDMAN 2411 DIANA ROAD BALTIMORE MD 21209-1525 |
| 3 | ALLIANT TECHSYSTEMS ATTN C CANDLAND L OSGOOD R BECKER 600 SECOND ST NE HOPKINS MN 55343 |
| 1 | US ARMY BENET LABORATORY ATTN SAM SOPOK SMCAR CCB B WATERVLIET NY 12189 |

NO. OF
COPIES ORGANIZATION

ABERDEEN PROVING GROUND

36 DIR USARL
ATTN: AMSRL-WT-P, A HORST
AMSRL-WT-PC,
R A FIFER
G F ADAMS
W R ANDERSON
R A BEYER
S W BUNTE
C F CHABALOWSKI
K P MCNEILL-BOONSTOPPEL
A COHEN
R CUMPTON
R DANIEL
D DEVYNCK
N F FELL
B E FORCH
J M HEIMERL
A J KOTLAR
M R MANAA
W F MCBRATNEY
K L MCNESBY
S V MEDLIN
M S MILLER
A W MIZIOLEK
S H MODIANO
J B MORRIS
J E NEWBERRY
S A NEWTON
R A PESCE-RODRIGUEZ
B M RICE
R C SAUSA
M A SCHROEDER
J A VANDERHOFF
M WENSING
A WHREN
J M WIDDER
C WILLIAMSON
AMSRL-CI-CA, R PATEL

INTENTIONALLY LEFT BLANK.

USER EVALUATION SHEET/CHANGE OF ADDRESS

This Laboratory undertakes a continuing effort to improve the quality of the reports it publishes. Your comments/answers to the items/questions below will aid us in our efforts.

1. ARL Report Number ARL-TR-965 Date of Report February 1996
2. Date Report Received _____
3. Does this report satisfy a need? (Comment on purpose, related project, or other area of interest for which the report will be used.) _____

4. Specifically, how is the report being used? (Information source, design data, procedure, source of ideas, etc.) _____

5. Has the information in this report led to any quantitative savings as far as man-hours or dollars saved, operating costs avoided, or efficiencies achieved, etc? If so, please elaborate. _____

6. General Comments. What do you think should be changed to improve future reports? (Indicate changes to organization, technical content, format, etc.) _____

**CURRENT
ADDRESS**

Organization

Name

Street or P.O. Box No.

City, State, Zip Code

7. If indicating a Change of Address or Address Correction, please provide the Current or Correct address above and the Old or Incorrect address below.

**OLD
ADDRESS**

Organization

Name

Street or P.O. Box No.

City, State, Zip Code

(Remove this sheet, fold as indicated, tape closed, and mail.)
(DO NOT STAPLE)